

OPEN ACCESS

Transmission electron microscopy characterization of NaAlH_4

To cite this article: P E Vullum *et al* 2008 *J. Phys.: Conf. Ser.* **126** 012015

View the [article online](#) for updates and enhancements.

You may also like

- [NaAlH₄ Nanoconfinement in a Mesoporous Carbon for Application in Lithium Ion Batteries](#)
L. Silvestri, A. Paolone, L. Cirrincione *et al.*
- [Effect of metal type and loading on hydrogen storage on NaAlH₄](#)
Mutsee Termtanun, Pramoch Rangsunvigit, Boonyarach Kitiyanan *et al.*
- [The kinetic enhancement of hydrogen cycling in NaAlH₄ by melt infusion into nanoporous carbon aerogel](#)
Robert D Stephens, Adam F Gross, Sky L Van Atta *et al.*



ECS
The
Electrochemical
Society
Advancing solid state &
electrochemical science & technology

DISCOVER
how sustainability
intersects with
electrochemistry & solid
state science research

Transmission electron microscopy characterization of NaAlH₄

Per Erik Vullum¹, Mark P Pitt², John C. Walmsley^{1,3}, Bjørn Hauback² and Randi Holmestad¹

1. Department of Physics, Norwegian University of Science and Technology (NTNU), 7491 Trondheim, Norway

2. Institue for Energy Technology, P.O. Box 40, 2027 Kjeller, Norway

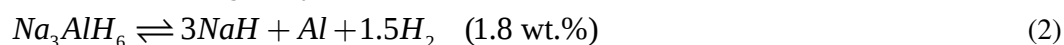
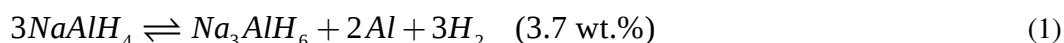
3. SINTEF Materials and Chemistry, 7465, Trondheim, Norway

Randi.Holmestad@ntnu.no

Abstract. Transmission electron microscopy (TEM) has been used to characterize NaAlH₄ doped with Ti, after H cycling. NaAlH₄ was shown to be highly unstable under the electron beam, and “knock on” damage lead to a decomposition of NaAlH₄ with Na and H evaporating from the sample. All Ti containing phases were stable under the electron beam. After H cycling, the Ti was present as a mixture of amorphous and crystalline Al_{1-x}Ti_x.

1. Introduction

Complex hydrides are promising materials for reversible hydrogen storage in proton exchange membrane fuel cells in cars [1]. In 1997 Bogdanovic and Schwickardi discovered that adding transition metals, such as Ti, to sodium alanate (NaAlH₄) enabled reversible hydrogen absorption at practical temperatures with enhanced kinetics [2]. A theoretical, reversible, storage capacity of about 5.5 wt.% H₂ can be achieved in a two-step decomposition, forming NaH and Al as the final products.



Much effort has been devoted to studying this process. Further progress depends on a thorough understanding of the state and catalytic role of the transition metal catalyst. Experimental techniques that have been applied include X-ray diffraction (XRD) [3-6], X-ray absorption spectroscopy (XAS) [7] and X-ray photoelectron spectroscopy (XPS) [7,8]. Density functional theory (DFT) calculations have studied possible bulk and surface substitutions of NaAlH₄ [9,10-14]. Theory [10] and experiment [1,5] confirm that bulk substitution of Ti into NaAlH₄ does not occur. While it is known that Ti is reduced to a metallic state during ball milling [8, 15-17], Ti containing phases remain invisible to most experimental techniques. X-ray diffraction [5,6,18,19] shows a shoulder on the high angle side of Al reflections, which has been attributed to Al₃Ti or Al_{1-x}Ti_x, but cannot account for all of the added Ti.

TEM analysis of NaAlH_4 systems has been limited [15,20-22] because; a) NaAlH_4 is unstable under the electron beam, and b) it is extremely sensitive to O_2 and H_2O . In this paper the possibilities and limitations of using TEM to characterize NaAlH_4 and Ti doped NaAlH_4 are carefully explored. The work has been performed to complement synchrotron x-ray diffraction studies.

2. Experimental

NaAlH_4 was purchased from Albermarle Corporation (LOT NO.#:22470404-01) and TiCl_3 was purchased from Sigma-Aldrich Chemicals Inc. (purities > 99.99 %). Materials were handled under inert atmosphere in a dry Ar glove box. NaAlH_4 powders with 10% TiCl_3 additive were prepared in 1 g quantities in a Fritsch P7 planetary mill, with ball to powder ratio of 20:1 and at 750 rpm, for 1 hour. Hydrogen cycling was performed in a Sieverts apparatus, rated to 200 bar and 600°C. Powders were removed after 2 H cycles.

TEM was performed with a JEOL 2010F operating at 200 kV, or with a Philips CM30 operating at 100-300 kV. Samples were loaded inside a glove box and transferred by two different methods: a) An oxygen tight transfer cover was used, with the cover being removed inside a glove bag attached to the holder entrance of the microscope. The glove bag was flushed with Ar (> 99.999 % purity). b) A Gatan environmental cell TEM holder was used. A vacuum gate valve allowed the sample to be withdrawn and isolated in the chamber during transfer. Method a) was most frequently used. Electron diffraction patterns were integrated by the ProcessDiffraction V_4.2.4 B software [23]. The inelastic background in the integrated diffraction patterns was subtracted by a combination of a four parameter exponential decay function and a third order polynomial.

3. Results and discussion

NaAlH_4 is highly unstable under the electron beam. Fig. 1 (a) shows an agglomerate of pure NaAlH_4 single crystals. Agglomerates decompose completely in a few seconds under a high electron flux, 200 keV electron beam. Na-rich particles, possibly with H, grow at the surface of the NaAlH_4 crystals and evaporate during decomposition. The final decomposition product is shown in Fig. 1 (b). Morphology, crystal structure and composition have changed during the decomposition. Electron dispersive spectroscopy (EDS), which is insensitive to H, showed only Al in the decomposition product.

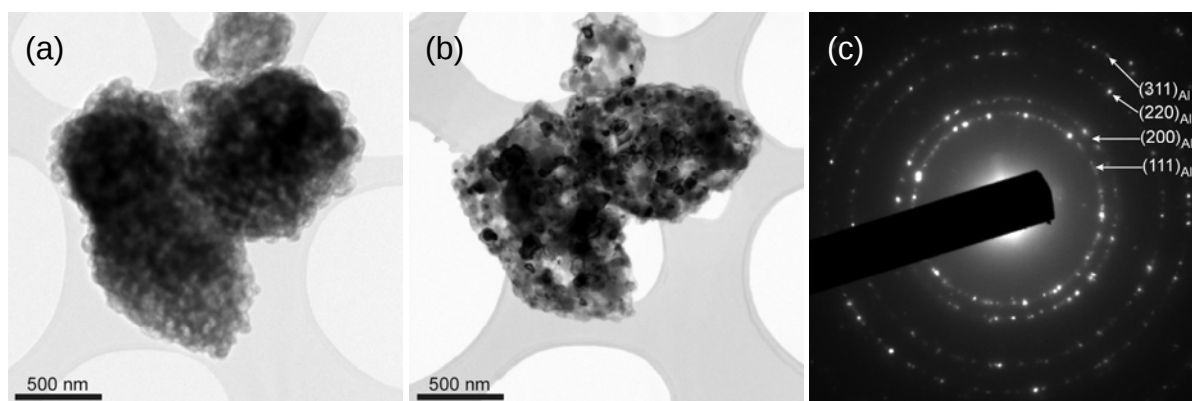


Figure 1. (a) Agglomerate of pure NaAlH_4 single crystals. (b) The same agglomerate after decomposition under the electron beam. (c) The diffraction pattern corresponding to Fig. 1 (b), showing only semi-continuous diffraction rings from Al.

Fig. 1 (c) shows the diffraction pattern corresponding to Fig. 1 (b). Semi-continuous diffraction rings from face centered cubic Al give only Bragg scattered intensity. It is concluded that the Na and

H have evaporated from the agglomerate, and the product is an agglomerate of Al crystallites with an average size of 40 nm. Reducing the electron beam energy from 200 to 100 keV and liquid nitrogen cooling of the sample gave only a very minor reduction of the decomposition rate, showing that the main cause of decomposition is “knock on” damage rather than heating. Use of a very low electron flux was the only way to preserve the alanate under the beam. Therefore, analysis has concentrated on bright field/dark field imaging and diffraction with a low electron flux beam. Long exposure times in the order of tens of seconds are required for image acquisition.

An oxidized alanate particle is shown in Fig. 2. The morphology is very different from the pure agglomerate shown in Fig. 1 (a) and the stability under the electron beam is high. Most of the Al and Na are bound in the form of stable oxides and no decomposition could be observed when focusing the beam. EDS showed an average composition with more than 50 at.% of O, compared to negligible O from the agglomerate shown in Fig. 1 (a). Comparison of Figures 1 (a) and 2 demonstrates the importance of careful sampling handling, avoiding exposure to air. Some earlier TEM studies of alanate systems, such as [20] and [22], are therefore of limited value since both morphology and O concentrations shown in these studies are comparable to the oxidized particle shown in Fig. 1 (d).

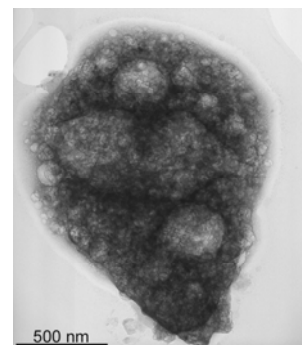


Figure 2. NaAlH₄ particle after exposure to oxygen.

Most of the added Ti was present as crystalline Al_{1-x}Ti_x solid solution, and a minor part was present as amorphous Al_{1-x}Ti_x. The semi-continuous crystalline Al_{1-x}Ti_x diffraction rings are dominant in the diffraction pattern in Fig. 3 (a). The amorphous Al_{1-x}Ti_x diffraction signal is only evident after integration of the diffraction pattern, as illustrated in Fig. 3 (b). In most of the integrated diffraction patterns, such as Fig. 3 (c), only crystalline Al_{1-x}Ti_x was present. Quantitative phase analysis by synchrotron X-ray diffraction showed that about 90 % of the Ti was found as crystalline Al_{1-x}Ti_x, with the remaining Ti present as amorphous Al_{1-x}Ti_x [24]. The primary amorphous halos of Al_{1-x}Ti_x were located at d-values of 2.21 Å. Diffraction peaks from NaCl and some Al is also present due to the reduction reaction between NaAlH₄ and TiCl₃ during ball milling [6].

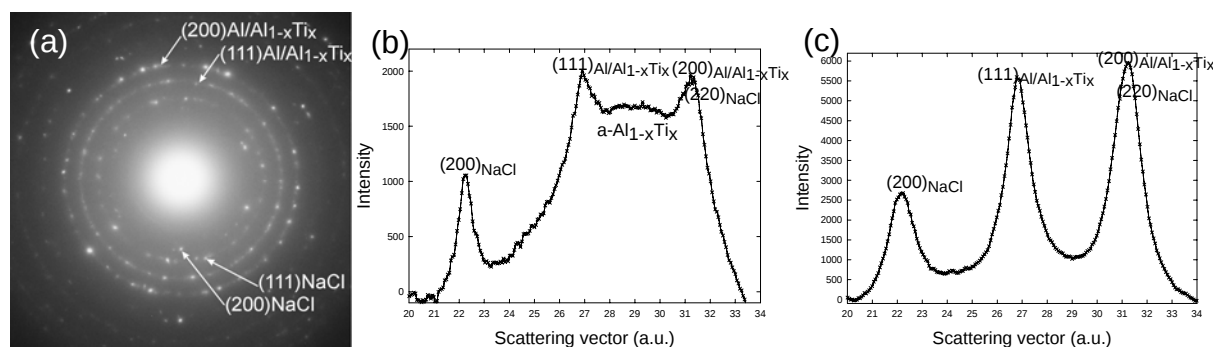


Figure 3. Diffraction patterns analysis. (a) shows that scattering from crystalline Al_{1-x}Ti_x is dominant. Integrated diffraction patterns show that some areas (b) have amorphous Al_{1-x}Ti_x in addition to crystalline Al_{1-x}Ti_x, and some (c) show only crystalline Al_{1-x}Ti_x.

4. Conclusions

NaAlH₄ is very sensitive to oxidation and very careful sample handling, without any contact with O₂ or H₂O, is absolutely essential in order to obtain trustworthy experimental data. In addition, the alanate decomposes rapidly under the electron beam due to “knock on” damage. Na rich particles grow at the surface of the NaAlH₄ grains, and both Na and H evaporate from the sample. Agglomerates of small face centered cubic Al crystallites are left behind after the decomposition.

However, it has been possible to perform detailed microstructural and crystallographic analysis that complement synchrotron diffraction data. The studies have also been extended to other transition metals, added as chlorides, fluorides or in the form pure nanoscopic powders.

Ti is traditionally not a very good catalyst for dissociation of molecular H_2 . Nevertheless, so far Ti has proved to be the best transition metal catalyst for reversible H storage in $NaAlH_4$. Bulk TiH_2 or $Al_{1-x}Ti_x$ are not expected to be good H_2 splitters. Further understanding of hydrogen storage behaviour in these materials will benefit from a detailed understanding of these phases, which are considerably more stable than the alanate under the electron beam and therefore amenable to TEM analysis.

References

- [1] F. Schüth, B. Bodanovic and M. Felderhoff, Chem. Commun. (2004) 2249.
- [2] B. Bogdanovic and M. Schwickardi, J. Alloys Comp. **253-254** (1997) 1.
- [3] K.J. Gross, G.J. Thomas and C.M. Jensen, J. Alloys Comp. **330-332** (2002) 683.
- [4] B. Bogdanovic, M. Felderhoff, M. Germann, M. Härtel, A. Pommerin, F. Schüth, C. Weidenthaler and B. Zibrowius, J. Alloys Comp. **350** (2003) 246.
- [5] H.W. Brinks, C.M. Jensen, S.S. Srinivasan, B.C. Hauback, D. Blanchard and K. Murphy, J. Alloys Comp. **376** (2004) 215.
- [6] C. Weidenthaler, A. Pommerin, M. Felderhoff, B. Bodanovic and F. Schüth, Phys. Chem. Chem. Phys. **5** (2003) 5149.
- [7] A. Leon, O. Kircher, M. Fichtner, J. Rothe and D. Schild, J. Phys. Chem. B **110** (2006) 1192.
- [8] A. Leon, D. Schild and M. Fichtner, J. Alloys Comp. **404-406** (2005) 766.
- [9] J. Iniguez, T. Yildirim, T.J. Udovic, M. Sulic and C.M. Jensen, Phys. Rev. B **70** (2004) 060101(R).
- [10] O.M. Løvvik and S.M. Opalka, Appl. Phys. Lett. **88** (2006) 161917.
- [11] O.M. Løvvik and S.M. Opalka, Phys. Rev. B **71** (2005) 054103.
- [12] J. Iniguez and T. Yildirim, Appl. Phys. Lett. **86** (2005) 103109.
- [13] C.M. Araujo, R. Ahuja, J.M. Osorio Guillen and P. Jena, Appl Phys. Lett. **86** (2005) 251913.
- [14] C.M. Araujo, S. Li, R. Ahuja and P. Jena, Phys. Rev. B **72** (2005) 165101.
- [15] M. Felderhoff, K. Klementiev, W. Grünert, B. Spliethoff, B. Tesche, J.M. Bellosta von Colbe, B. Bogdanovic, M. Härtel, A. Pommerin, F. Schüth and C. Weidenthaler, Phys. Chem. Chem. Phys. **6** (2004) 4369.
- [16] A. Leon, O. Kircher, J. Rothe and M. Fichtner, J. Phys. Chem. B **108** (2004) 16372.
- [17] J. Graetz, J.J. Reilly, J. Johnsen, A.Y. Ignatov and T.A. Tyson, Appl. Phys. Lett. **85** (2004) 500.
- [18] H.W. Brinks, B.C. Hauback, S.S. Srinivasan and C.M. Jensen, J. Phys. Chem. B **109** (2005) 15780.
- [19] A.G. Haiduc, H.A. Stil, M.A. Schwarz, P. Paulus and J.J.C. Geerlings, J. Alloys Comp. **393** (2005) 252.
- [20] A. Leon, O. Kircher, H. Rosner, B. Decamps, E. Leroy, M. Fichtner and A. Percheron-Guegan, J. Alloys Comp. **414** (2006) 190.
- [21] C.M. Andrei, J.C. Walmsley, H.W. Brinks, R. Holmestad, S.S. Srinivasan, C.M. Jensen and B.C. Hauback, Appl. Phys. A **80**, 709 (2005).
- [22] X.-D. Kang, P. Wang and H.-M. Cheng, J Appl. Phys. **100** (2006) 034914.
- [23] J.L. Lábàr, Ultramicroscopy **103** (2005) 237.
- [24] M.P. Pitt, P.E. Vullum, M.H. Sørby, D. Blanchard, S. Deledda, J. Walmsley, R. Holmestad, M.P. Sulic, C.M. Jensen, H. Emerich and B.C. Hauback, "Surface nano-precipitates in the transition metal enhanced $NaAlH_4$ system", to be submitted.